A Chemical Comparison of Freshwater Impoundments in Central Ohio

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By

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Abstract The many freshwater impoundments in the United States offer opportunities for the study of how water chemistry can vary due to geological settings and land use. Ten different small ponds from three counties in central Ohio were analyzed for dissolved constituents, including major ions, nutrients, and water isotopes. While some of the results were similar in all samples, significant variability was seen in several constituents, suggesting that environmental variability can affect the chemistry of the water in ponds, even those in close proximity to each other.

Acknowledgments

First and foremost, I have to thank my research supervisor, Professor W. Berry Lyons. Without his assistance and dedicated involvement in every step throughout the process, this thesis would have never been finished. I would like to thank you very much for your support and understanding in this project.

I would also like to thank Susan Welch and Elsa D. Saelens for performing the analyses of my samples. The time they put into the lab was essential in me getting my data, and I greatly appreciate their hard work, without which none of the data in my Results section would be possible.

I would also like to show gratitude to many members of the staff of the School of Earth Sciences with whom I've worked and who have helped me in obtaining my education over the past two years. I would especially like to thank my adviser, Dr. Anne Carey, whose patient guidance and advice was essential in my seeking an education in the Earth Sciences at The Ohio State University. I show my sincerest gratitude to Dr. John Olesik, whose quality instruction in data analysis class provided me with the skills I needed to complete much of the computer work that was necessary in writing this thesis. Finally, I would like to thank Dr. Michael Barton, Dr. Terry Wilson, Dr. Loren E. Babcock, Dr. Andréa G. Grottoli, and Dr. Lawrence A. Krissek for the valuable instruction they've provided me in the Earth Science classes that was essential to my ability to work on this project.

In spring 2013 and autumn 2013, I attended Columbus State Community College to take my introductory Geology classes. Jeff Richardson and Sherry Weisgarber provided me with quality instruction that helped me greatly in my pursuit of a Geology degree, and I thank them greatly for that.

Finally, I would like to thank my family and friends for their great amount of support they provided me in my life and education. Without their personal support none of my goals would be possible.

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Introduction

Small, artificial impoundments are a very common alteration to the landscape of the United States, and they have increased in the last century (Renwick 2006). Built for a variety of different purposes, they are a significant factor in the hydrologic landscape, with up to 9 million of them capturing and storing about 25% of the runoff in the continental US. Despite their abundance, they have been the focus of very little research by the scientific community, as much more focus has been centered on much larger bodies of fresh water (Renwick 2006).

Many environmental factors control the chemical characteristics of pond water. These factors include the local soil type, the source and flow path of the water that feeds the impoundment, the anthropogenic activities in the surrounding land, and local climate. The effects of these processes may affect the waters suitability for human consumption and aquaculture. The chemical analysis of fresh water from small impoundments is useful not only for determining its quality for drinking and aquaculture, but it can also give important information as to the nature of the geochemical processes that take place in the surrounding environment and the landscape practices that impact the water body itself.

In this study, samples of water from various ponds in central Ohio were collected and analyzed for a number of solutes, including nutrients, major cations, and major anions. The geochemical results were then compared to environmental and geomorphological factors to determine the sources of variation within the data.

Samples were collected from ten different small ponds, (all less than 1 acre in area). While all of the ponds were situated near human activity, the frequency and proximity of such activity varied, with some ponds located in urban environments, and others in rural ones. It is hypothesized that because some processes affecting the geochemistry will have greater consequences than others, the aquatic chemistry of these ponds will vary, even if the ponds themselves are geographically very close. It is further hypothesized that these differences can be correlated to differences in the environmental settings of the ponds.

Methods

The ponds from which samples were collected are in Franklin, Licking, and Perry Counties (Figure 1). Sampled ponds varied in surface area, from approximately 1000 square feet to about 1 acre, and all of them were in locations where the environment was heavily modified by man, either in parks or near buildings. The slopes of the banks were all 30° or less, and surface runoff was the most common source of water. A detailed description of each pond sampled is given in Table 1.

All ten samples were analyzed for major ions, nutrients, silica, and stable isotopes of oxygen and hydrogen. Samples were collected on May 22, 2014 and May 29, 2014, and within 10 days of collection were filtered through 0.1μm pore-size Nucleopore^{tm} membrane filters in the Lyons laboratory at The Ohio State University. The samples were then parsed into different aliquots for later analysis. The major cations and anions were measured using a Dionex Ion Chromatograph; the nutrients, including dissolved Si, were analyzed using a Skalar wet chemistry analyzer, and the isotopes, δD and δO, were analyzed using a Picarro Cavity Ringdown Spectrometer. The precision and accuracy of each measurement is shown in Table 2. The bicarbonate (HCO_3^-) concentrations were determined by subtracting the dissolved anion equivalents from the dissolved cation equivalents as outlined in Lyons et al. (2012):

$$HCO_3^- = 2Ca^{2+} + 2Mg^{2+} + Na^+ + K^+ - 2SO_4^{2-} + Cl^-$$

Results and Discussion

N and P concentrations

Phosphorous and nitrogen are important to the growth of plants, and concentrations of these nutrients are most likely to be a limiting factor in the growth of this important base of an aquatic ecosystem (Boyd 1998). Too much of these nutrients in ponds may cause eutrophication, which greatly decreases the level of dissolved oxygen in the water and negatively affecting its quality for aquaculture and for animal life (Hem 1985). Excess nitrogen in drinking water can cause major health problems such as methemoglobinemia, a blood disorder that affects young babies. Agricultural practices and sewage discharge are the main sources of contamination of these two elements (Domenico and Schwartz 1990) In addition, N input can also come from fossil fuel combustion (Hem 1985).

Nitrogen enters freshwater impoundments in various ways, including through the atmosphere in molecular form (N_2) through the water supply, through fixation in organic compounds by algae and bacteria, or by addition from pollution as noted above. The various ways nitrogen is transformed by biological activity is summarized in Figure 2. All ten ponds were analyzed tested for the following three common forms of nitrogen in water: NO_2^-, NO_3^-, and NH_4^+.

Nitrate enters pond water through rain, and may be removed by plants or microbes. Microbes remove nitrate when facilitating decomposition of organic matter in a process called nitrate reduction. This method of nitrate removal is very important when the organic matter has high C/N ratio (low nitrogen). Nitrite may be produced by the oxidation of ammonia in process called nitrification, or by the reduction of nitrate in a process called denitrification (Boyd 1998).

Ammonium may be lost from pond water to usage by plants, or by the process of denitrification, a conversion to nitrate by bacteria. Ammonium may also diffuse into the air when concentrations are high, as the atmospheric concentrations are usually very low. It can be added to the pond water as a byproduct of decomposition of organic matter with a low C/N ratio, especially under anoxic and suboxic conditions, and also may be added to the water by excretion from living organisms (Boyd 1998).

Phosphorous concentrations in ponds are usually quite low, but it can be introduced to ponds through a variety of ways including the input from the atmosphere, runoff, inflow, and fertilization (Boyd 1998). Phosphorous pollution from runoff can be a large problem, due to the elements tendency to attach to soil particles (Hem 1985).

Although plants and bacteria may take up phosphorous, the fate of most phosphorous in ponds is to reside in the bottom sediments and even the phosphorous taken up by the phytoplankton and plants will eventually meet this fate. Phosphate in water may react with aluminum, iron, or calcium in the sediments, depending on the pH of the soil. Calcium phosphates can be precipitated from water at pHs above 6, while aluminum phosphates are dominant in acidic soils. Phosphate can readily be absorbed into Fe oxides/hydroxide minerals. Because of its loss to soils, phosphates, are often added to fertilized ponds, but 70% of phosphorous originates from feeds or fertilizers eventually becomes part of the sediment (Boyd 1998).

As seen in Table 3, there was a significant degree of variation in the dissolved fixed nitrogen (NO_2^-, NO_3^-, and NH_4^+) and phosphate concentrations in the pond samples. There was more variation in the phosphate than for nitrate, with standard deviations of 0.364 μmoles/L for nitrate and 0.368 μmoles/L for phosphate, respectively.

The covariance between total N and total P is 0.124, indicating a very slightly positive relationship between the two. This low covariance can be expected, since although these nutrients share some of the same sources, their concentrations in water are affected by different chemical attributes which would vary depending on biological and geological factors.

The Carmack pond was exceptional in its high nutrient content, contributing significantly to the overall variance in the samples. The standard deviations for nutrients for the other nine ponds are 0.278 μmoles/L, for phosphate (a 28% difference), and 0.233 μmoles/L for nitrates (a 45% difference.) The high concentrations of nutrients in this pond would most likely be explained by its location in the middle of a well-maintained lawn, which probably receives fertilizer. The pond is also frequently visited by geese, whose droppings contain a significant amount of N and P. It has been shown, however, that goose droppings tend to fall quickly to the bottom of the pond, therefore not significantly contributing to the water chemistry until sediment is stirred up (Uncless 2007)

It was observed that the Carmack pond contained a significant amount of floating organic matter, so it can be inferred that much sediment was stirred up from the bottom, a consequence of the ponds shallowness, as well as the placement of a fountain in the middle. The small size could also be a factor in the pond's high dissolved nutrient concentrations, as the nutrients would get concentrated in the pond's small volume. The Dawes pond, which had the most goose excrement in its surroundings, also had high dissolved nutrient concentrations. Both of these ponds are different than the Woodside pond, which although

showing evidence of geese presence, had the lowest dissolved nutrient concentrations. There can be no strong conclusions drawn from this study as for the significance of avian fecal matter leading to the nutrient concentrations in these impoundments.

Nitrate-nitrite/Ammonium

Ammonia is produced in freshwater by decomposition of organic matter by heterotrophic bacteria (Quirós 2003), and as a waste product of metabolism by aquatic organisms (Cole 1994.) The ammonium may be taken up by plants or used by bacteria in the process of nitrification, where it is oxidized to nitrite and then to nitrate:

$$NH_4 + 1½\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O \text{ (Boyd 1998)}$$

It can be concluded that waters with high ammonium to NO_2^-+NO_3^- ratios have a significant amount of bacterial decomposition of organic matter. As seen in Figure 3, this appears to be the case in all of the ponds analyzed, with the Langdon pond showing the most dominant NH_4^+ concentration, and the Autumn pond having the lowest NH_4^+ concentration. In Figure 3 there is evidence that COTC South pond water is diluted COTC Central water, as concentrations of both forms of nitrogen are lower in this pond. It should be noted that the NH_4^+ concentration of the COTC South pond was ~100% greater than in the COTC Central pond, while the NO_2^-+NO_3^- difference was a mere 18%. This suggests that dilution is not the only reason that the COTC Central pond had lower NH_4^+ values, and indicates that the latter had higher levels of bacterial composition of organic matter.

The Carmack results showed the lowest NH_4^+/ (NO_2^- +NO_3^-) ratio, a result that could be explained by the presence of a fountain in the center of the pond. The greater amount of oxygen added to the water by the aeration by the fountain may cause an increase in the oxidation of the NH_4^+ ion, and therefor increasing the NO_2^-+NO_3^- concentrations. It is evident from the results of NH_4^+ and NO_2^-+NO_3^- that anoxic decomposition of organic matter is significant in all ponds tested.

Nitrogen and Phosphorous Ratio

Figure 4 shows the PO_4 to total fixed nitrogen ratio, as well as the Redfield ratio, which describes the ratio of nitrogen to phosphorous in aquatic plankton (Lenton 2000). Any deviation from this ratio indicates an excess of either of these two elements relative to plankton uptake. While some of the ponds were slightly enriched in phosphorous, most were nitrogen enriched, and the Langdon pond showed the greatest nitrogen enrichment. The use of phosphorous in fertilizers could be an explanation for the excess phosphorous in the COTC

and Dawes ponds, while the excess nitrogen in the Langdon pond could be the result of runoff enhanced in nitrogen from the nearby highway. Overall, there does not seem to be any apparent pattern for the deviations from the Redfield ratio, and further study would be necessary to determine with certainty why individual ponds have an excess of nitrogen or phosphorous, and what the ultimate sources of these nutrients are.

Major ions

The dissolved major cations and anions directly measured in the study are listed in Table 4. The relative abundance of major ions in freshwater impoundments is subject to much regional variation and environmental control. Some ions enter water through the atmosphere, either by solutes in precipitation or dry fallout, and some are added by overland flow, groundwater input, leaching through soils, and the chemical weathering of the landscape (Cole 1994). Sodium, potassium, calcium, magnesium, chloride, sulfate, and bicarbonate make up the bulk (95% or more by weight) of dissolved ions in most natural waters (Boyd 1998).

Bicarbonate is generally the main anion in fresh water (Faure 1991). Chloride can also be a major component of the total dissolved anions present, and although there are natural sources, Cl^-, is also a major indicator of anthropogenic activities (Dailey et al. 2014). The sulfate ion is the most common anion after carbonate, and its presence in high concentrations in fresh water is a significant indicator of industrial pollution, such as sulfur rich gases from fossil fuel combustion, industrial processes, and runoff. Calcium and sodium sulfate present in ancient marine sediments may also be a major contributor to high sulfate waters, as well as the presence of metal sulfides in local bedrock such as black shale. (Cole 1994).

The concentrations (mmoles/L) of sodium and chloride are listed in Table 5. The standard deviations in the concentrations are 1.58 mmoles/L for the chloride ion and 1.16 mmoles/L for the sodium ion, and the means are 1.24 mmoles/L for the chloride ion, 0.93 mmoles/L for the sodium ion. It should be noted that these statistics are greatly affected by the outlier of the group, the Langdon pond, whose concentrations were much higher than in the other sampled ponds. The standard deviations for the samples, Langdon pond not included, are 0.73 mmoles/L for chloride ion and 0.43 mmoles/L for the sodium ion, and the means are 0.79 mmoles/L for the chloride ion, and .0.56 mmoles/L for the sodium ion. The high Na^+ and Cl^- concentrations in the Langdon pond can be explained by its close proximity to a highway, as the application of deicing salt would cause an increase in sodium chloride in runoff water. Dailey et al. (2014) have noted an increase in both Na^+ and Cl^- in many Ohio

rivers over the past 50 years due to road deicing activities. This could have significant implications for ponds and lakes that are near roads and highways. It should be noted that even though the Na^+ and Cl^- concentrations in the Langdon ponds were exceptional in comparison to the other samples, they were not high enough to be considered unacceptable for either aquaculture or human consumption (Table 6).

The molar ratio of Na^+ and Cl^- is 1.63, not 1:1 as would be expected by the dissolution of NaCl in water. As shown in Figure 5, two of the ponds did indeed exhibit a near perfect 1:1 ratio of sodium and chloride ions: the Spencer and Crandell ponds, which are very close geographically. COTC South, COTC central, and Langdon all exhibited a much greater concentration of Cl^- than sodium. The use of CaCl as road and sidewalk de-icing salt might be an explanation for this anomaly in the COTC ponds, as the Ca^+ concentrations were also higher. This stands in contrast to the Langdon pond, where it can be inferred through the low concentration of the Ca^{2+} ion that CaCl road salt was not the source of excess Cl^-, and there must be another source. Magnesium and potassium chloride salts may also contribute to fresh water chloride concentration (Hunt et al. 2012).

Chloride may be present in evaporate minerals found in sedimentary rocks, and the weathering of these rocks may be a significant contributor to its solution in water. Shales may contain chloride that may be leached from them when exposed near from the surface. (Hem 1985) It is not clear what the source of this excess Cl^- is, and this should be the focus of future research.

Another noteworthy observation from Figure 5 is the relationship of the Na^+ and Cl^- concentrations for the COTC South pond compared to COTC Central; both the sodium and chloride ions are slightly less concentrated in COTC South. This result is to be expected, as the COTC South receives some of its water supply from drainage of the COTC Central pond, and therefore should have the chemical composition of diluted COTC Central water.

The results for Na and Cl in this study support the idea that surrounding land use is the main contributor in the variation of these two elements in pond water.

Water Isotopes

Information about the source, residence time, and evaporation history of water can be inferred through the stable isotopes ^{18}O and the hydrogen isotope deuterium (D) (Faure 1991) It is necessary to measure and report these isotopes by their relative abundance compared to a standard. This is done using the using the equation:

$$\delta D \text{ or } \delta O = ((R_{sample} - R_{standard})/R_{standard}) \times 1000$$

where δ is the deviation from the standard, reported as permil (‰), and R is the specific isotope ratio for the sample and the standard. (Faure 1991).

Determination of the D and ^{18}O isotope ratios were utilized to determine if the water in each pond is meteoric, and if any of the ponds have undergone evaporation. It can be inferred that a sample whose isotopic composition falls directly on the meteoric water line has been largely unaffected by isotopic fractionation due to evaporation.

Deviations from the meteoric water line indicate fractionation processes that can be identified from the sample's position on the line. Since evaporation causes enrichment of heavier isotopes, (i.e., the lighter isotopes evaporate faster), an evaporation signature can be determined if values do not fall on the meteoric water line of $\delta D = 8\delta O^{18} + 10$ (Craig 1961). The amount of evaporation a body of water has undergone can be determined by its position on this line (Faure 1991).

It is evident from Figure 6 that all but three of the sampled impoundments lay very near the meteoric water line, and therefore, do not show significant evaporation. The most evaporated pond (Langdon) is geographically very far from the COTC ponds, which were also heavily evaporated, but very close to the Spencer and Crandell Ponds, which both fell very close to the water line. Processes that could be responsible for the high evaporation of these three ponds may be due to longer residence time of the water or even perhaps the input of partially evaporated shallow groundwater. Future work could be tied to gaining a better understanding of the overall hydrology of these ponds, which could greatly aid in the interpretation of the water isotope data.

Silica: Groundwater vs. Surface Water

The majority of the ponds analyzed are fed by runoff, either from buildings or land drainage, and this is partially evident in the results. Groundwater tends to have higher dissolved Si concentrations than surface water, so it can be inferred that groundwater-fed ponds would have higher concentrations (Hem 1985). Ponds fed by surface water should be expected to have higher Cl contents (Hunt et al. 2012). Figure 7 shows dissolved Si vs. chloride ion in the samples. The spring-fed Spencer pond contains $9.8 * 10^{-2}$ mmoles/L dissolved Si, which is slightly higher than the mean of $6.45 * 10^{-2}$ M, and significantly higher than the median of $3.2 * 10^{-2}$ mmoles/L. It is interesting to note that this is not the highest concentration observed, as both the COTC and the Crandell ponds have higher dissolved Si content than the Spencer pond, with the Crandell pond having the highest concentrations. While the higher concentrations of dissolved Si in the COTC ponds could originate from the

dissolution of concrete, the high dissolved Si concentration in the Crandell pond was unexpected considering the source of the water (mostly surface runoff).

As shown above, evidence for the dilution of the COTC Central water in the COTC South pond is evident in the dissolved Si concentrations, as the concentration is indeed lower in the South pond.

Carbonate Solution

Calcite ($CaCO_3$), aragonite ($CaCO_3$), and dolomite $CaMg(CO_3)_2$ are minerals found in sedimentary rocks in Ohio, and in water these minerals can dissolve via H_2CO_3 to form 2 bicarbonate ions for each calcium or magnesium ion (Hen 1985).

Figure 8 shows the $Mg^{2+} + Ca^{2+}$ vs HCO_3, with a line representing a perfect 1:2 ratio. Only half of the samples fall on this line while the others indicate excess bicarbonate. The bicarbonate ion is present in other salts, such as K_2CO_3 and Na_2CO_3, but these are relatively rare (Hunt et al. 2012). The presence of excess HCO_3^- in the samples suggest very strongly that the source is from the weathering of alumnosilicate minerals such as:

Primary silicate + $H_2CO_3 \rightarrow$ clay/oxide mineral + HCO_3^- + dissolved Si + dissolved cation

Conclusions

The results of this study demonstrate a large variation in all parameters tested, with geographic location not a significant factor in these variations. Differences in environmental surroundings, and perhaps differences in local anthropogenic activities were apparently the cause of this chemical variation, and in some cases, the environmental processes responsible could be determined with reasonable certainty. In the Langdon pond the use of road salt is a likely explanation for the high Na^+ and Cl^- concentrations, and the smaller concentrations of nutrients and ions in the COTC South pond compared to COTC Central can be linked to fact that much of its water comes from the latter pond and has been diluted. Other results, such as the deviation from the meteoric water line in a few others, cannot be explained without further study.

A comparison of the ions found in the samples with acceptable standards for human consumption and acceptable and ideal standards for aquaculture is provided in Table 6. It is notable that only ammonium concentrations would be deemed unsafe for human consumption, and this was the case in only two of the ponds. Many concentrations were outside the ideal range for aquaculture, however, with dissolved Si and ammonium being outside of the range in the majority of the samples.

It is notable that while concentrations of major ions or nutrients varied considerably, there were some striking similarities in the results suggesting that that some similar processes may be occurring in the local watersheds many of the ponds. For example, there was a considerable amount of variability in the concentrations of Na^+ and Cl^-, but all of the ponds either showed a 1:1 ratio or an excess of Cl^-. Similar results were seen in the NH_4^+/ (NO_2^- +NO_3^-) results, as all ponds showed excess NH_4^+ relative to the nitrate + nitrite. These similarities among geographically different ponds suggest similar landscape and/or anthropogenic attributes.

One factor that showed little evidence of affecting the water chemistry was the major source of water, i.e. groundwater vs. runoff water feeding the ponds. The Spencer pond, fed primarily by groundwater, did not show any different results than runoff-fed impoundments. A greater number of groundwater-fed ponds would be needed to be analyzed, however, to make any conclusions as to what effect water source has on pond chemistry.

Suggestions for Future Work

The analyses performed for this study are only a fraction of what could be done to collect information on these environments. Measurements of pH, dissolved oxygen, water clarity, and many other dissolved ions can provide much more valuable information that gives clues to the biogeochemical and hydrological processes taking place in these impoundments.

Much more future work could be done. Because there would be seasonal variations in natural processes that affect the water chemistry, samples could be collected through the year, so that a time-series could be established. These results in the geochemistry could be correlated to both geochemical and hydrological data. Because chemical weathering of rocks is a strong contributor to the concentrations of many ions in the water, ponds with different types of sub-surface lithologies could be analyzed and compared. Ponds surrounded by glacial till might give different results than those underlain by carbonate or siliciclastic rocks, such as those in the unglaciated portion of the state.

The results of this study suggest that anthropogenic sources may greatly influence pond geochemistry more than do natural ones. For example, the fountain in the Carmack pond, and the proximity of the Langdon pond to the nearby highway seemed to be important sources of chemical variation, while the presence of geese in the Woodside and Dawes ponds, and the groundwater source of the Spencer pond did not seem to be so important. Further studies could be conducted to test the hypothesis that anthropogenic activities are more important by examining a number of ponds in urban settings and comparing them to those from more remote ones.

Freshwater impoundments in the United States are not only a significant part of the landscape, but they also provide many opportunities for the study of natural hydrological processes, as well as provide some clues as to how mankind is affecting the environment. Artificial impoundments are always going to be present, and they provide extensive opportunities to study the natural processes that affect the landscape.

References Cited

Boyd, CE. 1998. Water Quality in Ponds for Aquaculture. Alabama Agricultural Experiment Station, Auburn University, Alabama, 482 pp.

Cole, GA. 1994. *Textbook of Limnology*. Fourth Edition. Prospect Heights: Waverly Press, Inc.

Craig, HS. 1961. Isotopic variations in meteoric waters. Science. 133. pp 1702

Dailey, KR, Welch, KA, Lyons, WB. 2014. Evaluating the influence of road salt on water quality of Ohio rivers over time. Applied Geochemistry. Vol 47, pgs 25-35.

Domenico, PA, Schwartz FW. *Physical and Chemical Hydrogeology***.** New York: John Wiley and Sons, 1990.

Faure, G. 1991. *Principles and Applications of Inorganic Geochemistry*. New York: Macmillan Publishing Company.

Hem, JD. 1985. *Study and Interpretation of Chemical Characteristics of Natural Water.* 3rd edition. US Geological Survey Water-Supply Paper 2254.

Hunt, M, Herron, E, and Green, Linda. 2012. Chlorides in fresh water. URI Watershed Watch. March 2012.

Ganeshalingam, S, Jeyadevan, JP, Kuganathan, N. 2012. Physicochemical analysis of pond water samples from selected areas in Valukkai Aru Drainage Channel, Jaffna, Sri Lanka. Water Research and Development. Vol. 2 | No.1&2 | 12-23 | January-August | 2012

Lenton, TM, Watson, AJ. 2000. Redfield revisited: regulation of nitrate, phosphate, and oxygen in the ocean. Global Geochemical Cycles, vol. 14, No.1, pgs. 225-248.

Leslie, D, Welch, K and Lyons, WB. 2014. Domestic water supply dynamics using stable isotopes and d-excess, Journal of Water Resource and Protection, 6, 1517-1532.

Lyons, WB, Welch, KA, Gardner, CB, Jaros, C, Moorhead, D, Knoepfle, JL, Doran, PT. 2012. The geochemistry of upland ponds, Taylor Valley, Antarctica. Antarctic Science, 24 (1), 3-14.

Quirós, R. 2003. The relationship between nitrate and ammonia concentrations in the pelagic zone of lakes. Limnetica 22(1-2): 37-50.

Renwick, WH, Sleezer, RO, Smith, SV. 2006. Small artificial ponds in the United States: Impacts on Sedimentation and Carbon Budget. Proceedings of the Eighth Federal Interagency Sedimentation Conference, April 2-6, 2006, Reno, Nevada, USA.

Unckless, RL, Makarewic, JC. 2007. The impact of nutrient loading from Canada Geese (*Branta canadensis*) on water quality, a mesocosm approach. Hydrobiologia.586:393–401

Welch, KA, Lyons, WB, Whisner, C, Gardener, CB, Gooseff, MN, McKnight, DM, Priscu, JC. 2010. Spatial variations in the geochemistry of glacial meltwater streams in the Taylor Valley, Antarctica. Antarctic Science 22(6), 662–672

Appendix A

Figures

Figure 1. Locations of ponds sampled. Ponds that were very close together are not separated on the map.

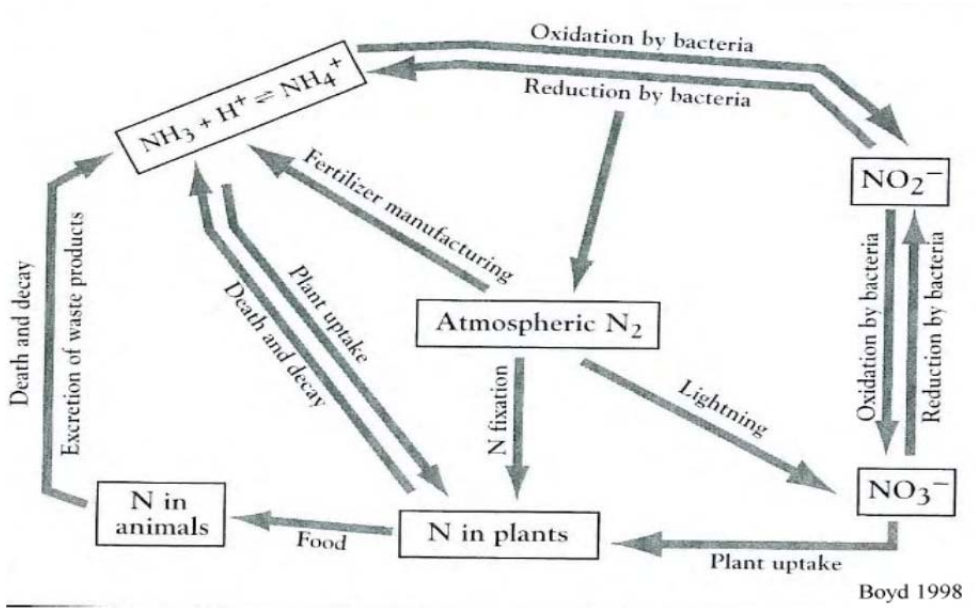

Figure 2. Cycle of nitrogen in aquatic systems. Nitrogen can undergo many different transformations and processes once it enters an aquatic system.

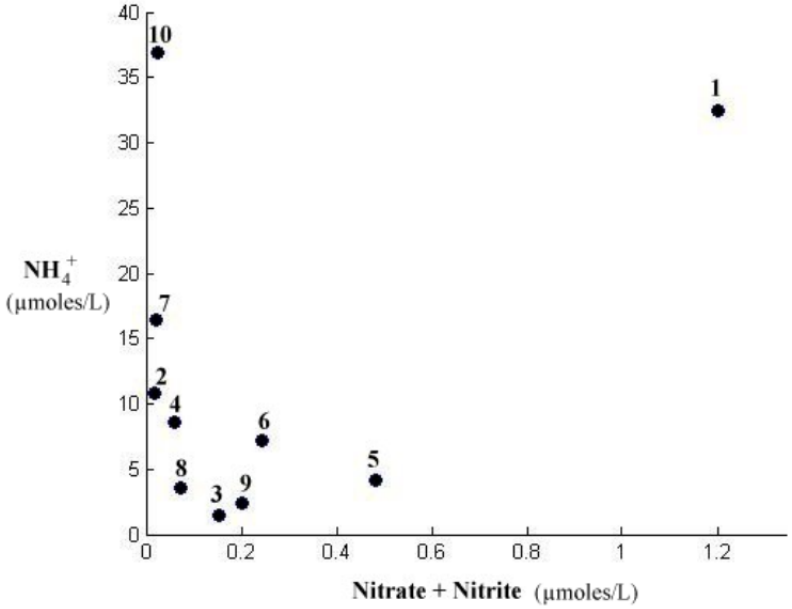

Figure 3. Ammonium vs. Nitrate-nitrite. The ammonium ion is dominant in all ponds, but least dominate in the Carmack pond.

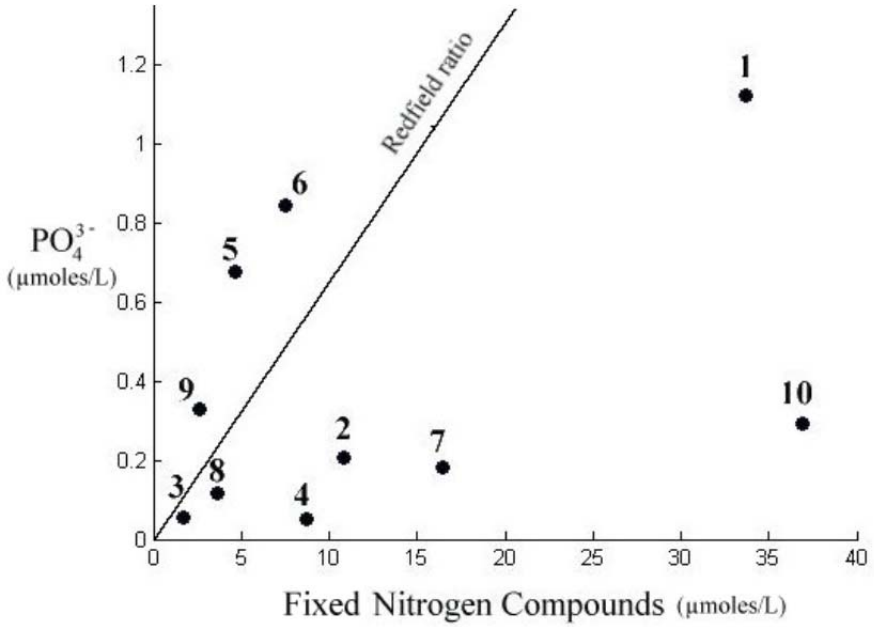

Figure 4. PO_4^{3-} vs Nitrogen. The Redfield ratio is indicated by a solid line. Samples that deviate from this ratio have excess PO_4^{3-} or N.

1. Carmack	4.Woodside	7. TG Evans	10. Langdon
2. Spencer	5. Dawes	8. Crandell	
3. Autumn	6. COTC Central	9.COTC South	

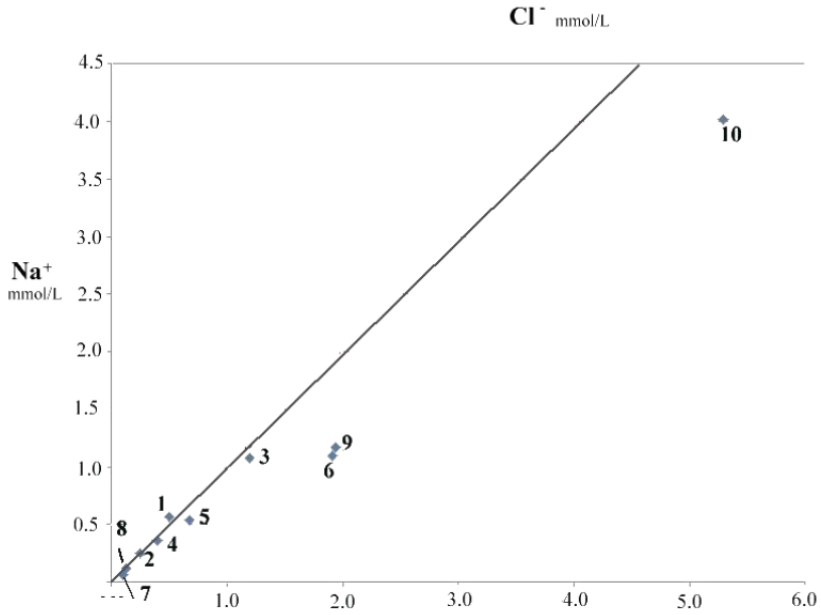

Figure 5. Na^+ vs Cl^-. A 1:1 molar ratio is indicated by the solid line. As seen in the figure, several of the ponds showed an excess of chloride.

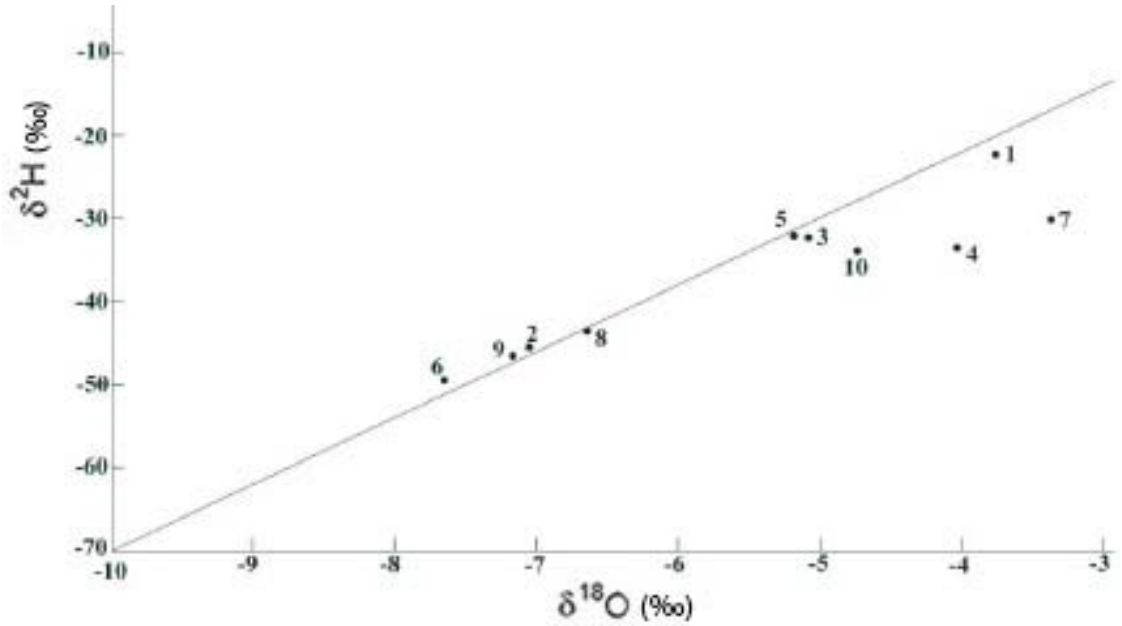

Figure 6. $\delta^{18}O$ vs δD. The solid, diagonal line is the meteoric water line. Several of the ponds deviate from this line, indicating that evaporation has taken place.

1. Carmack	4.Woodside	7. TG Evans	10. Langdon
2. Spencer	5. Dawes	8. Crandell	
3. Autumn	6. COTC Central	9.COTC South	

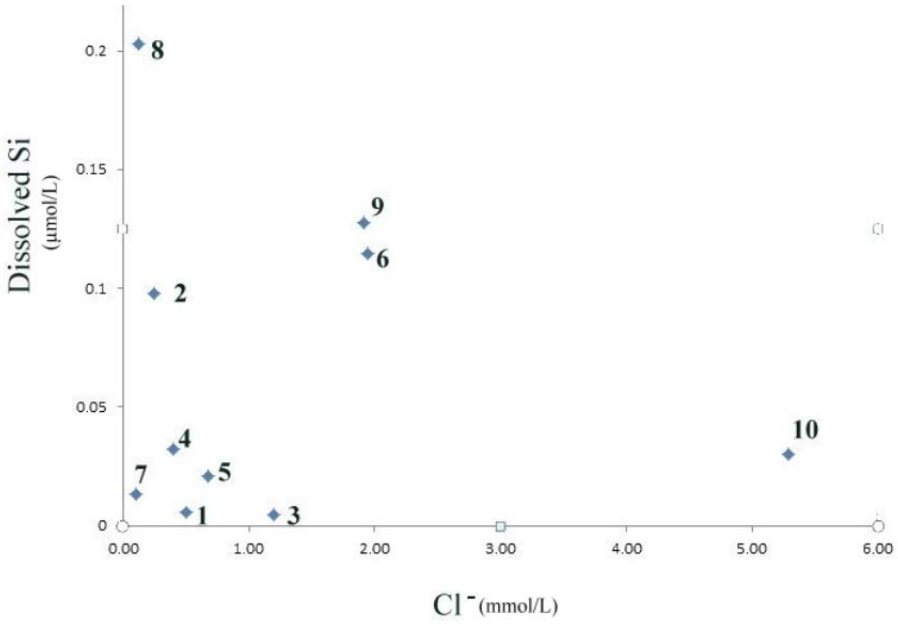

Figure 7. Dissolved Si vs. Cl^-. Ponds fed by groundwater should be expected to have higher dissolved Si concentrations.

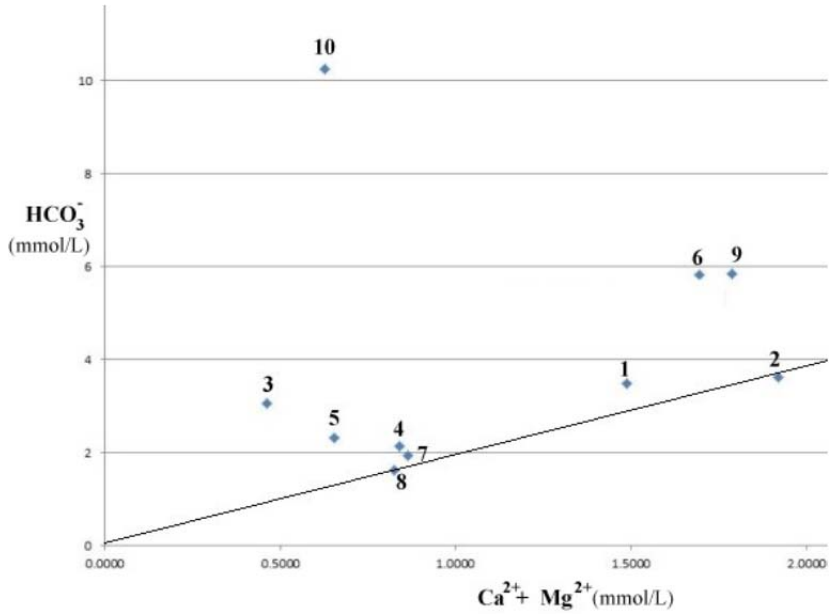

Figure 8. HCO_3^- vs. Ca^{2+}+ Mg^{2+}. A solid line showing a 1:2 ratio of Ca^{2+}+ Mg^{2+} to bicarbonate is shown diagonally. Many of the ponds have an excess of bicarbonate.

1. Carmack	4.Woodside	7. TG Evans	10. Langdon
2. Spencer	5. Dawes	8. Crandell	
3. Autumn	6. COTC Central	9.COTC South	

Appendix B

Tables

Table 1. Features of the sampled ponds. The sampled ponds showed variation in their environmental settings that could affect their water chemistry.

Pond Name	Approx. Size	Location and environment	Slope of Bank*	Feed type	Other features
Carmack	1500 sq ft.	OSU Campus	Shallow	Surface runoff	Significant aquatic vegetation, and floating organic matter
Spencer	½ acre	Rural home, northern Perry County	Steep	Groundwater, Spring	Continuous, year-round inflow and outflow
Autumn	1000 sq. ft.	Urban Building Complex, Northern Perry County	Moderate	Building runoff	Embankment is somewhat elevated from surrounding land
Woodside Green	1 Acre	Urban Park, Norwest Columbus	Shallow	Building runoff, lawn runoff	Big Walnut creek close by. Many geese.
Dawes Arboretum	1/5 acre	Rural Park, Central Licking County	Steep <30 degrees	Surface Runoff	
COTC Central	¼ acre	Urban Building Complex, Central Licking County	Shallow	Surface runoff, building runoff	Continuous feeding in summer months through air conditioning system
TG Evans	2000 sq ft.	Abandoned Quarry, Northern Licking County	Shallow	Groundwater, surface runoff	Situated between two much larger ponds
Crandell	1500 sq ft.	Rural home, Northern Perry County	Shallow	Surface runoff	Farm land in drainage area
COTC South	1/5 acre	Urban Park, Central Licking County	Moderate	Surface runoff, drainage from Cotc Central	Receives drainage water from Cotc Central
Langdon	¼ acre	Rural home, Northern Perry County	Steep	Surface, building runoff	Highway nearby with moderate traffic

*** Shallow less than 10 degrees, Moderate 10-20, Steep, 20-30 degrees**

Table 2. Precision and accuracy in measurements. The major cations and anions were measured using a Dionex Ion Chromatograph; the nutrients, including dissolved Si, were analyzed using a SKALAR wet chemistry analyzer, and the isotopes, δD and δO, were analyzed using a Picarro Cavity Ringdown Spectrometer.

Analyte	Accuracy* (mg/l^{-1})	Precision† (mg/l^{-1})
Na^{+}	1.6	< 1
Ca^{2+}	23.5	< 1
Mg^{2+}	15.3	< 1
K^{+}	2.6	< 1
Cl^{-}	0.2	< 1
SO_4^{2-}	0.2	< 2
HCO_3^{-}	ND	14
NH^{+}	8.6	ND
NO_3^{-} + NO_2^{-}	2.0	< 2
PO_4^{3-}	4.9	< 3
δO^{18}	ND	< 0.5 (ppm)
δD	ND	< 1.0 (ppm)
Si	0.1	< ±10%

*Percentage difference from USGS certified standards M-212 & N-124

Ⱨ From Welch et al. (2010); Lyons et al. (2012) and Leslie et al. (2014) and all in % variation reported as a coefficient of variation except δO^{18} and δD which are in parts per mill.

Table 3. Fixed nitrogen and phosphate in the sampled ponds. A significant amount of variation is seen in the concentrations of these nutrients.

Ponds	Fixed Nitrogen (μmoles/L)	PO_4 (μmoles/L)
Carmack	33.7	1.1
Spencer	10.8	0.2
Autumn	1.7	.05
Woodside	8.7	.05
Dawes	4.6	0.7
COTC Central	7.5	0.8
TG Evans	16.4	0.2
Crandell	3.6	0.1
COTC South	2.6	0.3
Langdon	37.0	0.3

Table 4. Major ion concentrations from the sampled ponds.

Pond	Li (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Si (ppm)	Sr (ppm)	Ba (ppm)	SO_4 (ppm)	Na (ppm)	Cl (ppm)
Carmack	0.002	6.48	15.32	56.72	0.16	1.791	.050	35.1	13.73	12.7
Spencer	0.007	2.97	14.73	76.77	2.75	0.107	.044	37.8	6.04	8.89
Autumn	0.0005	0.50	5.02	18.46	0.14	0.038	.017	7.69	26.01	42.4
Woodside	0.0005	2.59	7.90	33.53	0.90	0.091	.171	17.7	8.25	14.1
Dawes	0.0007	2.24	10.30	26.09	0.59	0.053	.014	12.9	12.87	24.0
COTC Central	0.004	1.09	25.71	67.66	3.22	0.189	.044	34.0	28.04	69.0
TG Evans	0.0008	4.27	10.19	34.49	0.38	0.066	.020	3.73	1.66	3.52
Crandell	0.0004	1.04	13.59	32.93	5.71	0.054	.017	14.5	3.01	4.51
COTC South	0.004	1.20	26.36	71.44	3.59	0.174	.016	36.4	26.31	67.8
Langdon	0.002	0.32	17.95	24.99	0.84	0.062	.013	15.7	96.4	188

Table 5. Molar Concentrations of Cl^- and Na^+. The molar ratio of the ions is not a perfect 1:1 ratio, and the Langdon pond shows by far the highest concentrations.

Ponds	Cl^- (mmol/L)	Na^+ (mmol/L)
Carmack	0.50	0.57
Spencer	0.25	0.25
Autumn	1.19	1.08
Woodside	0.40	0.36
Dawes	0.68	0.54
COTC Central	1.94	1.17
TG Evans	0.10	0.07
Crandell	0.13	0.13
COTC South	1.91	1.10
Langdon	5.30	4.02

Table 6. Comparison of results with selected standards for human consumption and aquaculture. Maximum concentrations for human consumption are based on World Health Organization (WHO) standards. Ideal ranges for aquaculture are taken from Boyd (1998).

Ion	Maximum Concentration for human consumption (1) (ppm)	Ideal ranges for aquaculture (2) (ppm)	min/max in Samples (ppm)	# of samples above range for human consumption	# of samples outside range for aquaculture
SO_4	500	5-100	3.7/37.8	0	1
K	NA	1-10	.32/6.5	0	2
PO_4	.1	.005-.2	< .1	0	0
Na	200	2-100	1.7/96.4	0	1
Ca	200	5-100	18.5/76.8	0	0
Mg	150	5-100	5.0/26.4	0	0
Cl	250	1-100	3.5/188	0	0
Si	NA	2-20	.14/5.71	0	6
HCO_3	NA	0-20	2.7/11.7	0	0
NH_3	0.5 ppm	<.1	.04/.63	2	6

1: Ganeshalingan et al. 2012
2. Boyd 1998